

Electric Conductivity of Cured Arylhydrazino-N,N'-(4,4'-1,1'-Sulfonyl Biphenylene) Bis-Maleimide-Epoxy Resins

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Arylhydrazino-bismaleimide (AHBM) have been prepared by the Michael addition reaction of various phenyl hydrazine derivatives with N,N'-(4,4'-1,1'- sulfonyl biphenylene) bis-maleimide (SBM). These arylhydrazino bismaleimides (AHBM) were employed for curing commercial epoxy resins. The curing behaviour of commercial epoxy resin with these AHBM compounds using 2-methyl imidazole as a catalyst has been monitored using differential scanning calorimetry. Glass fibre reinforced composites of the epoxy-AHBM system have also been prepared and characterized mechanically and chemically. The electrical conductivity of all unreinforced epoxy-AHBM cured products were measured at room temperature and it was found that the produced cured materials having good chemical resistance, good mechanical strength and low conductivity.

Key Words: Electric conductivity, Arylhydrazino bis-maleimide, Epoxy resins.

INTRODUCTION

In continuation of our research work on novel bismaleimide-epoxy resin system developed for glass reinforced composites, the work presented here with synthesis of other bismaleimides. Epoxy resins are extensively used in a number of applications like moulding, adhesives, paints, powder coating etc.¹ Epoxy resins in their procured state are colourless to yellowish brown viscous liquids. The viscous state of epoxy resins is quite stable and is not affected by weather at room temperature. Cured epoxy resins are produced by the addition of curing agents (hardeners), such as diamines, anhydrides, thiols, etc.¹ Epoxy hardeners containing hydrazine groups have been reported², including hydrazine derivatives of carboxylic acid³⁻⁶. In the present communication, we used an arylhydrazine derivative of bis-maleimide as the hardener, with an epoxy resin to form a cured network.

EXPERIMENTAL

Materials and Synthesis: Commercial epoxy resin, *i.e.*, diglycidyl ether of

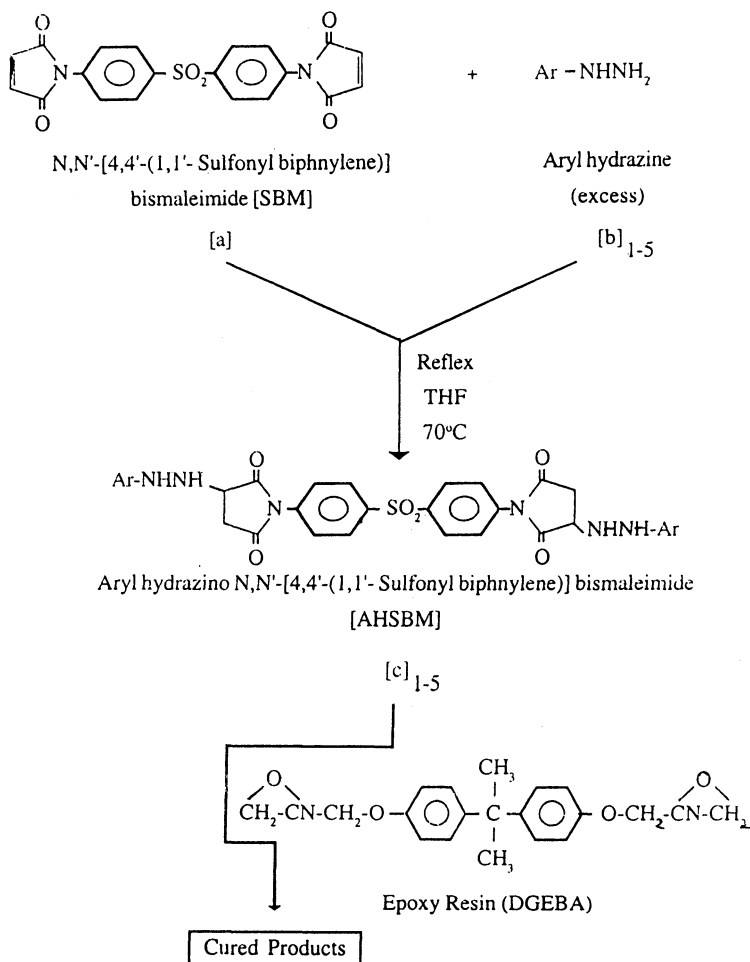
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bisphenol-A (DGEBA), was obtained from Sympol Products Pvt. Ltd., Ahmedabad, India. The specifications of this epoxy resin are: epoxy equivalent 190–200; viscosity, 4–10 P; density, 1.15–1.17 g/cm³.

Arylhydrazine derivatives, *viz.*, phenyl hydrazine, 4-chlorophenyl hydrazine, 4-bromophenyl hydrazine, 4-methylphenyl hydrazine and 4-methoxyphenyl hydrazine were obtained from Chiti Chem., Baroda, India and used as received. N,N'-(4,4'-1,1'-sulfonyl biphenylene) bis-maleimide (SBM) was prepared by the reported method⁷.

All arylhydrazino-N,N'-(4,4'-1,1'-sulfonyl biphenylene) bis-maleimide (AHSBM) derivatives (**Scheme-1**) were prepared by previously reported litera-



Scheme-1. Ar = (1) phenyl, (2) 4-chlorophenyl, (3) 4-bromophenyl, (4) 4-methylphenyl, (5) 4-methoxyphenyl.

ture⁸. The unreinforced epoxy resin-AHSBM products were prepared by mixing epoxy resin (1 mol) and AHSBM derivatives (0.25 mol)⁸ (used for DSC study) and heated for 2 h at curing temperature. The products were crushed, washed with hot water and then air dried.

Composite Fabrication: The glass-fibre reinforced composites (GRC), based on epoxy resin-AHSBM system, were prepared⁹ by mixing a stoichiometric ratio of the epoxy resin and AHSBM (40% weight of total glass-fibre cloth) in THF. The resulting mixture was mixed well for 10 min. The suspension was then applied with a brush onto a 150 mm × 150 mm epoxy compatible fibre glass cloth and the solvent was allowed to evaporate. Once dried, the ten prepregs were stacked one on top of another, pressed between steel plates coated with a teflon film, released and compressed in a flat platen under about 0.5 MPa. The prepregs were cured by heating the press at 170–180°C for 12 h in an air-circulating oven. The laminate so obtained was cooled at room temperature before the pressure was released. Test specimens were made by cutting the laminates and machining them to their final dimension.

FTIR and DSC: FTIR analysis was done on a Perkin-Elmer-983 spectrophotometer. Curing of the epoxy resin with AHSBM compounds was monitored by DSC using a DuPont 900 DSC at a heating rate 10 K/min. The sample for this investigation was in the range of 4 to 5 mg and an empty cell was used as a reference. Thermogravimetric analysis (TGA) of all AHSBM epoxy cured and uncured products was carried out on a DuPont thermobalance in air at a heating rate of 10 K/min.

Mechanical and chemical properties: All the mechanical and chemical properties were measured on three individual specimens and average results have been documented.

Flexural strength test: The measurement of flexural strength of the composites was carried out on a Universal Instron testing machine, model number A-74.37, at room temperature according to the method of ASTM D-770. The crosshead speed was 100 mm/min.

Compressive strength test: The compressive strength was measured according to an ISO method. The sample size was 12.5 × 12.5 mm.

Impact strength test: The measurements were made with an Izod type impact tester at room temperature according to the testing method of ASTM D-256.

Hardness test: The Rockwell hardness was measured according to ASTM D-785. The sample size was 25 × 25 mm.

Chemical resistance test: The chemical resistance test was measured according to the ASTM D-543 method. The sample size was 20 × 20 mm.

Electrical Conductivity: For the electrical conductivity measurements, a pellet of the polymer sample was prepared by pressing a finely powdered and dried sample under hydrostatic pressure¹⁰ at 20,000 psi for 2 min.

A uniform thin layer of silver paste was applied to both sides of the pellet to provide electrical contacts. Average diameter and thickness of each pellet were measured. The pellet was firmly pressed between two circular metal discs functioning as electrodes. The other ends of the electrodes were passed through the pellet holder for connections. The resistance of the pellet was measured by a

million megohm meter (RM 160 MK III A, BPL, India). The specific conductivity (σ) of the pellet was estimated by the usual relations from the resistance of the pellet and its dimensions. The electrical conductivity (σ) of the polymer sample was measured at room temperature. The test conditions are: diameter of pellet (d), 1.015 cm; surface area of pellet (A), 0.808 cm²; thickness of pellet (l) = 0.19 cm; source voltage (V_s) = 8.5 V; input resistance (R) = 109 ohm.

RESULTS AND DISCUSSION

The DSC study of the unreinforced epoxy-AHSBM was adopted to establish the curing temperature for bulk curing. Examination of all the DSC scans of the epoxy-AHSBM system shows a broad curing exotherm in the temperature range of 70–200°C. The exotherm was characterized by noting the T_p obtained by drawing a tangent at the start of the exotherm and at the final exotherm temperature T_f . The heat of curing (ΔH) was obtained from the area under the exotherm. The results of DSC scans for the curing of all the AHSBM resins in the presence of a catalyst are summarized in Table-1. All the samples have T_p values in the range of 100–180°C depending upon the nature of the system. The heat of curing indicates complete reaction in the presence of catalyst.

TABLE-1
DSC CURING STUDY OF AHSBM-EPOXY RESINS

Sample*	Cure onset temperature (T_i) (°C)	Peak temperature (T_p) (°C)	Final temperature (T_f) (°C)	Activation energy (E_a) (kcal/mol)
1	132	178	188	34.50
2	120	155	170	29.20
3	100	128	180	31.20
4	70	102	150	34.60
5	125	166	195	37.20

*Stoichiometric proportion of AHSBM-DGEBA epoxy resin used.

IR spectrum (not shown here) of all the AHSBM-epoxy unreinforced systems reveals that the discernible difference observed between cured product and parent compounds was a band due to the epoxy ring at 910 cm⁻¹ in resin which almost vanished in the spectra of all the epoxy-AHSBM cured products, indicating that curing was through the epoxy group and —NHNH— group of AHSBM, as expected.

The TGA data of all cured products are given in Table-2. Cured products start to decompose at around 250°C and the rate of decomposition increases between 300 and 500°C. The results of TGA show that the cured products lose almost 90% of their mass at 600°C, which indicates that the cured products have good thermal stability.

TABLE-2
TGA OF AHSBM-EPOXY RESINS

Sample*	% weight loss at various temperatures (°C)				
	250	300	400	500	600
1	3	13	33	67	95
2	3	10	34	68	91
3	5	15	34	68	93
4	4	16	30	60	90
5	5	14	36	64	92

*Stoichiometric proportion of AHSBM-DGEBA epoxy resin used.

The glass-reinforced composites of epoxy-AHSBM resins have a density in the range of 1.8 to 2.0 g/cm³. Chemical resistance test reveals that all composites have remarkable resistance towards organic solvents and concentrated HCl. However, treatment with concentrated NaOH changes the thickness by a small amount and weight by about 1.3%. Mechanical properties of all composites reveal that all the composites have good mechanical strength and chemical resistance data furnished (Table-3).

TABLE-3
MECHANICAL AND ELECTRICAL PROPERTIES OF GLASS-REINFORCED
COMPOSITES BASED ON AHSBM-EPOXY (EQUIVALENT RATIO) SYSTEMS

Sample*	% change on exposure to 25% (w/v) NaOH		Density (g/cm ³)	Flexural strength (MPa) (ASTM D- 770)	Compressive strength (MPa) (ISO method)	Impact strength (MPa) (ASTM D-256)	Hardness (R) (ASTM D-785)
	Thickness	Weight					
1	1.1	1.1	1.92	195	190	245	141
2	0.9	1.1	1.83	200	195	220	139
3	0.9	1.0	1.88	185	180	210	141
4	1.1	1.1	1.90	195	190	265	140
5	1.2	1.1	1.90	210	195	245	138

*Stoichiometric proportion of AHSBM-DGEBA epoxy resin used.

Examination of data reveals that electrical conductivity of each of AHSBM-epoxy resin cured materials at room temperature is found to be in the range of $2.3-4.2 \times 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$, indicative of low conductivity.

Comparison of the properties of produced cured products with those of other cured products by using same epoxy resin reveals that the produced cured products have slightly higher mechanical strength but the end cured products are dark coloured. So the pigmentation could not be achieved. This would be

disadvantageous; otherwise the produced system could be applicable commercially.

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REFERENCES

1. H. Lee and K. Neville, *Hand Book of Epoxy Resin*, McGraw-Hill, New York (1978).
2. C.Y. Glenda, US Patent 4,816,531; *Chem. Abstr.*, **111**, 196058c (1989).
3. O.P. Baraban, A.E. Ryskina, L.V. Efimenco and S.Z. Sintezi, *Unglevodorod Kauehakov Naikh Osnove M.*, 121 (1979); *Zh. Khim. Abstr.*, 24T600 (1979).
4. D.P. Kochetov, F.R. Gritsenko, V.K. Grishchenko and Yu.L. Spirin, *Vysokomol Soedin*, **21A**, 2171 (1979).
5. D. Aelony, *J. Appl. Polym. Sci.*, **13**, 227 (1969).
6. H.H. Levine, US Patent 3,014,009 (1959).
7. J.V. Crivello, *J. Polym. Sci.*, **14**, 159 (1976).
8. S.V. Patel and J.M. Daraji, *Oriental J. Chem.*, **17**, 299 (2001).
9. ———, *Ultra Scientist Physi. Sci. (India)*, **14**, 97 (2002).
10. M.S. Patel, *J. Macromol. Sci. Phys.*, **325**, 57 (1986).

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